Regulation of Air Toxics Under the 1990 Clean Air Act Amendments[1/]

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I.   Introduction

The 1990 Clean Air Act Amendments significantly revised the regulation of hazardous air pollutants under § 112. The old § 112 required EPA to identify hazardous air pollutants and promulgate health-based emission standards for each pollutant. The new § 112 requires EPA to regulate categories of sources using technology-based emission standards. Section 112 now specifically identifies 189 hazardous air pollutants, directs EPA to promulgate a list of the "major" and "area" source categories that emit those pollutants, and specifies a schedule within which EPA must promulgate emission standards for all source categories.

EPA has only just begun to implement the new air toxics provisions. This fall EPA promulgated a list of approximately 170 major and area sources including chemical manufacturers, polymers and resins producers, pharmaceutical producers, oil and natural gas producers, and petroleum refineries and proposed a schedule for regulating those sources. Synthetic organic chemical manufacturers will be among the first sources to be regulated. EPA's proposed hazardous organics national emission standard for hazardous air pollutants (hazardous organics NESHAP or HON) may require synthetic organic chemical manufacturers to reduce emissions of as many as 149 hazardous air pollutants.

This paper will provide an overview of the new air toxics provisions including the HON, the early reductions program which enables sources to delay compliance with new regulations, and the modification provision which may compel sources to comply with new emission standards even sooner than otherwise required.

II. Overview of § 112

The new § 112 establishes a list of 189 hazardous air pollutants that must be regulated under the air toxics program. Clean Air Act ("CAA") § 112(b). The statute directs EPA to issue a list of categories and subcategories of "major" and "area" sources that emit those pollutants. Last summer, EPA promulgated a list of approximately 170 source categories to be regulated. See 57 Fed. Reg. 31,591 (July 16, 1992).

Section 112 distinguishes between "major" and "area" emission sources. A "major source" is defined as "any stationary source or group of stationary sources located within a contiguous area and under common control that emits or has the potential to emit considering

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controls, in the aggregate 10 tons per year or more of any hazardous air pollutant or 25 tons per year or more of any combination of hazardous air pollutants." CAA § 112(a)(1). An "area source" is any source of hazardous air pollutants that is not a major source. CAA § 112(a)(2).

Once a source is on the list, it will be subject to technology-based emission standards. EPA must establish emission standards for every source category on the list by the year 2000. For major sources, the emission standards will be based on the maximum degree of reduction in air toxic emissions achievable based on the best technology currently available for the source category in question (maximum achievable control techology or MACT). Existing sources subject to MACT standards will have to achieve the average emissions limitation achieved by the best performing 12 percent of the existing sources or the average emission limitation achieved by the best performing five existing sources if less than 30 sources are in the category. New sources must meet the emissions limitation achieved by the best performing plant.

EPA must also promulgate technology-based emission standards for area sources. The Act directs EPA to establish standards for area sources based on "generally available control technology" (GACT). In practice, this standard will probably be less stringent than the MACT standard for major sources.

The statute establishes a timeframe within which EPA must promulgate these emission standards and then requires EPA to promulgate a more specific schedule based on its own source category list. Section 112(e) requires EPA to promulgate emission standards for 40 source categories by November 15, 1992, for 25 percent of all source categories by 1994, for 50 percent of all source categories by November 1997, and for the remaining source categories by November 15, 2000. EPA issued its proposed regulatory schedule in September 1992. See 57 Fed. Reg. 44,147 (Sept. 24, 1992). According to the proposal, synthetic organic chemical manufacturers must be regulated by November 15, 1992. EPA missed this deadline but hopes to promulgate a final rule by the end of 1993.

While the Amendments added the concept of technology-based standards, they did not completely abolish health-based emission standards. By November 1996, EPA must investigate and report to Congress on the risks to public health remaining, or likely to remain, after application of MACT standards and make recommendations for legislation necessary to control those risks. CAA § 112(f)(1). The Agency must adopt residual risk-based standards if any source in a source category presents a risk to the maximum exposed individual of more than one in one million (1×10^{-6}). The risk-based standards must protect public health with an ample margin of safety and prevent adverse environmental effects. Furthermore, the Act contains a savings provision for the health-based emission standards promulgated under the old § 112. See CAA § 112(q). EPA must, however, review and revise those pre-1990 standards, if appropriate, before the year 2000.

III.   The Early Reductions Program

Sources may delay compliance with MACT standards by participating in the early reductions program under § 112(i). CAA § 112(i)(5); 57 Fed. Reg. 61,970 (December 29, 1992). An existing source can qualify for a six-year compliance extension by voluntarily reducing hazardous air pollutant emissions by 90 percent (95 percent for particulates) before EPA proposes a MACT standard applicable to the source. Sources subject to MACT standards

proposed before 1994, such as synthetic organic chemical manufacturers, may participate in the early reductions program by making an enforceable commitment to meet program requirements by January 1, 1994. Sources that qualify for the extension will be subject to an alternative emission limitation (AEL) which will be included in the sources' title V operating permit.

To encourage sources to participate, EPA has attempted to build some flexibility into this program. The final early reductions rule uses a flexible definition of "source" to enable a facility to chose whether to enroll the entire facility in the program or limit participation to certain process units provided that the emission reductions constitute significant reductions from the entire facility. The source may also chose the baseline year for calculating reductions, but it may be no earlier than 1987 unless the source can show that an earlier year (1985 or 1986) is more representative. Finally, a source may take credit for reductions taken for any reason, whether voluntary or involuntary.

Most sources interested in participating in the early reductions program may apply through the state's title V permit program. Sources subject to MACT standards proposed before 1994, however, may have to apply for a "specialty permit" through EPA because state title V permit programs will not likely be in place before January 1, 1994, the date by which those sources must make an enforceable commitment in order to participate in the program.

IV. Modifications & Reconstruction of "Major Sources"

While the early reductions program enables sources to delay compliance with MACT standards, some sources may become subject to MACT standards sooner than would otherwise be expected because of § 112's modification provision. Under § 112(g), once a state operating permit program is in place, if a modification to a "major source" is proposed and that modification would increase actual emissions of any hazardous air pollutant by more than a de minimis amount, then the modification cannot begin until the facility demonstrates that it will meet the MACT for existing sources. Because EPA has not yet defined "source" for purposes of MACT standards, it is unclear whether a modification would trigger MACT compliance for the specific emission point being modified or for the plant as a whole.

This modification provision differs from that under the new source review program in that not all modifications will trigger the rule, only those that will cause more than a de minimis increase in actual emissions. Section 112(a)(5) defines "modification" as "any physical change in, or change in the method of operation of, a major source which increases the actual emissions of any hazardous air pollutant emitted by such source by more than a de minimis amount or which results in the emission of any hazardous air pollutant not previously emitted by more than a de minimis amount." EPA has not yet defined de minimis for purposes of this section.

Even if the modification would cause more than a de minimis increase in emissions, sources making modifications can avoid demonstrating compliance with MACT standards by offsetting any increase in hazardous air pollutants by decreasing other hazardous emissions. More specifically, a physical or operational change that would otherwise fit the definition of modification will not be considered a "modification" if the owner or operator of the source shows that the "increase in the quantity of actual emissions of any hazardous air pollutant from

such source will be offset by an equal or greater decrease in the quantity of emissions of another hazardous air pollutant (or pollutants) from such source which is deemed more hazardous."[y]

One final point to note about the modification provision is that although it does not apply until after operating permit programs are in place, it has the effect of imposing MACT standards on sources even before EPA establishes MACT standards for that particular category or subcategory. In those cases, the emission limitation will be set on a case-by-case basis. CAA § 112(g)(2)(A).

While modifications under this provision may subject sources to MACT standards for existing sources, a major source that is reconstructed will be subject to MACT standards for new sources. The 1990 Amendments do not define "reconstruction," but EPA is likely to use the definition under the new source review provisions as a starting point for defining the term.

V.   The Hazardous Organics NESHAP

The HON is the first major set of technology-based emission standards proposed under § 112 as amended and is therefore the best indication of how EPA plans to implement the new air toxics program. 57 Fed. Reg. 62,608 (Dec. 31, 1992). For example, this rule will indicate how EPA defines "source" in the context of MACT standards, how EPA determines the MACT floor, and how costs will be factored into the definition of MACT.

A.   Definition of "Source"

The definition of "source" is important for a number of reasons. First, it describes the emission points to which each standard will apply. It is also important for defining the MACT floor, that is, the minimum emission level the source must meet, and finally, it is important for determining whether a particular source is a "major source" (i.e., whether the plant emits more than 10 tpy of any air toxic or 25 tpy of any combination of air toxics).

EPA has not adopted a general definition of "source" for purposes of § 112 but has indicated that it plans to define "source" within each MACT standard.[y] The HON as proposed defines "source" broadly. Under the HON, "source" will include all the process vents, storage vessels, transfer racks, wastewater collection and treatment operations, and equipment leaks in the organic hazardous air pollutant emitting chemical manufacturing processes that are located in a single facility covering a contiguous area under common control. The HON will apply to chemical manufacturers that produce one or more of the synthetic organic chemicals listed in the

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[y] CAA § 112(g)(1)(A). EPA is in the process of developing regulations for the offset provision. The rule should include a ranking of the 189 hazardous air pollutants based on their effects on human health and the environment.

The offset provision applies only in the context of modifications and will not protect major sources from MACT standards once EPA has promulgated them for the source category.

[y] Sources should note that the definition may or may not be the same as the definition of "source" for purposes of the title V permit program.

rule and have an organic hazardous air pollutant as either: (1) a product, by-product, co-product, or intermediate or (2) a reactant.[5]

B. Definition of MACT

How EPA defines MACT is also important. For purposes of the HON, EPA determined the MACT floor by looking at each type of emission point, as opposed to the source as a whole, and developed a "reference control technology" (RCT) for each emission point that would satisfy the statutory maximum achievable control technology requirement. Affected sources will have to limit regulated emissions to the level that would be achieved using that RCT. How to achieve the emission limitations is up to each source. It may apply the RCT or another technology that will achieve the same standard. According to EPA, this standard takes into consideration the cost of controls.

The HON also allows sources to use emissions averaging to achieve the required emission limitations. This provision allows a source to average emissions from two or more emission points to achieve the overall emission reduction that would be achieved using the RCT. Therefore, by overcontrolling certain emission points, a source can undercontrol other emission points if the average satisfies the standard.

These requirements will be phased in over time. While the statute allows up to three years for compliance with air toxics emission standards, the HON will require certain process units to comply within six months of promulgation and others to comply within a year and a half after promulgation.

VI. The General Duty Clause

At least one regulatory provision of § 112 creates immediate obligations for industry. Congress enacted § 112(r) to prevent and detect accidental releases of hazardous air pollutants. This section applies to all owners and operators of stationary sources that produce, process, handle, or store certain "extremely hazardous" substances and imposes a "general duty" to prevent and respond to accidental releases of those substances.

The statute requires EPA to promulgate a list of not less than 100 substances "which, in the case of an accidental release, are known to cause or may reasonably be anticipated to cause death, injury, or serious adverse effects to human health or the environment."[6] Section 112(r) imposes an affirmative duty on owners and operators "to identify hazards which may result from [accidental] releases using appropriate hazard assessment techniques, to design and maintain a

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[5] The equipment leak provisions of the HON will also apply to the following sources: styrene/butadiene rubber production, polybutadiene production, chlorine production, pesticide production, chlorinated hydrocarbon use, pharmaceutical production, and miscellaneous butadiene use.

[6] CAA § 112(r)(3). The statutory deadline for this list was November 15, 1992. EPA missed this deadline but hopes to propose a list along with the regulations under § 112(r) in 1993.

safe facility taking such steps as are necessary to prevent releases, and to minimize the consequences of accidental releases which do occur." CAA § 112(r)(1).

Although the statute requires EPA to promulgate regulations under this provision by November 1993, this "general duty" appears to be self-implementing. That is, it can be used as a basis for enforcement actions by EPA, even in the absence of any implementing regulations defining what steps are needed to comply with this "general duty."

VII. Implementation of the Air Toxics Program

The air toxics regulations will be implemented by the states under the title V operating permit program. Once the states have developed an EPA-approved operating permit program, all major sources under § 112 will be required to obtain a title V permit which specifies the applicable emission standards.

All major sources of hazardous air pollutants will be required to apply for a title V operating permit within 12 months of implementation of the state permit program, and those sources will have to report their air toxics emissions in their permit applications even if they are not yet subject to an emission standard under § 112. The title V permit rules require sources to describe in their permit application emissions of all "regulated air pollutants." "Regulated air pollutant" includes any air pollutant for which a § 112 standard has been established, regardless of whether the standard applies to the source submitting the permit application. That is, if a § 112 standard has been established for any source to limit emissions of a particular hazardous air pollutant, then all sources must report their emissions of that pollutant in their permit applications. See 40 C.F.R. § 70.2; 57 Fed. Reg. 32,295, 32,297 (July 21, 1992) (final title V permit rules). The list of "regulated air pollutants" for purposes of § 112 could become quite long very quickly; the HON alone may regulate as many as 149 of the 189 listed hazardous air pollutants.

VIII. Issues to Watch

In the next year, EPA will propose its general provisions under § 112 which will define basic terms and requirements that apply across MACT standards including monitoring, recordkeeping, and reporting requirements. EPA will also propose regulations under the modification provision, and in the next two years, EPA is scheduled to propose and promulgate MACT standards for over 40 source categories. Along with the HON, these rules will define the new air toxics program. Because the air toxics provisions of the statute leave many questions unanswered and because the way those questions are ultimately resolved can have a great impact on regulated entities, it will be important for industry to follow and participate these rulemakings.

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COAL CONVERSION AT THE K/T BOUNDARY: REMNANTS OF THE HAZARDOUS WASTE

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ABSTRACT

The occurrence of large amounts of two nonprotein amino acids, aminobutyric acid (AIB) and isovaline (ISOVAL), in sediments near the Cretaceous/Tertiary (K/T) boundary was originally attributed to remnants of a bolide collision. However, these two amino acids are derived from the same two hydantoins that were isolated in large amounts from gasifier quench water, and we hypothesized that the K/T amino acids originated from a natural coal gasification process involving intrusion of magma into a coal seam. Condensation of the resulting gases, including carbon dioxide, ammonia, hydrogen cyanide, and ketones formed the hydantoin precursors for the amino acids. The K/T AIB/ISOVAL ratio corresponds to that observed for the corresponding hydantoins in gasifier quench water. The ratio of the ketones (acetone and 2-butanone) resulting from pyrolysis of a large variety of coals is also consistent with the AIB/ISOVAL ratio, although much larger amounts of the ketones are generated from low-rank coals.

INTRODUCTION

At the close of the Cretaceous Period, a large number of species became extinct, most noteworthy, the dinosaurs. Many theories have been suggested to explain the mass extinction at the Cretaceous/Tertiary (K/T) boundary, including climate and land mass changes as well as collisions with a massive extraterrestrial object (bolide). The occurrence of nonprotein amino acids in sediments deposited before and after the K/T boundary was interpreted as evidence for an extraterrestrial event (1). Recently I established that the assumptions that led to that conclusion were erroneous, and that a more likely explanation for the occurrence of the amino acids, aminoisobutyric acid (AIB) and isovaline (ISOVAL), is that they formed from hydrolysis of hydantoins that were produced from coal-derived gases (2). This hypothesis is based on the finding of large amounts of hydantoins, mainly 5,5-dimethylhydantoin (DMH) and 5-ethyl-5-methylhydantoin (EMH), in condensate water from a coal gasification facility (3,4). The two major hydantoins (DMH and EMH) were present in concentrations of about 2000 and 500 mg/L, respectively, in condensate water from gasification of Indian Head lignite (4). Numerous other 5-substituted hydantoins were also identified at concentrations an order of magnitude smaller (3). The two major hydantoins produced as by-products of coal gasification are in fact those that generate AIB and ISOVAL on hydrolysis. Thus the AIB and ISOVAL isolated from the sediment samples may very likely have resulted from natural thermal processing of terrestrial coal sources via hydantoin formation and subsequent hydrolysis.

The K/T transition was accompanied by extensive magmatic intrusions and volcanic activity. Magmatic intervention in a coal seam may have generated the gases that condensed and reacted to form large amounts of the hydantoins. Many examples of thermal magmatic decomposition of coal have been reported in

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geological investigations of coals from various locations (5). In order to ascertain which intrusion sites might be candidates for the generation of the precursor components required for hydantoin synthesis, a relationship between the chemical evidence in the K/T or near K/T deposits and potential coal progenitors must be demonstrated. The purpose of this paper is to present data that relates to the issue of coal-derived precursors for the amino acids.

RESULTS AND DISCUSSION

The formation of hydantoins in the water from the slagging gasifier was demonstrated to have resulted from the complex Bucherer-Bergs reaction of ammonia, carbonate, hydrogen cyanide, and various ketones and aldehydes present in the gas cooling/condensing system (spray washer and tar-oil-water separator) of the gasifier and not from a high-temperature reaction in the gasifier itself (6,7). In the upper pyrolysis region of the slagging fixed-bed gasifier, hot gases produced in the high-temperature gasification zone heat the coal and release the ketones, as well as phenolics, alcohols, nitriles, and other volatile organic components. A large number of ketones are produced in coal pyrolysis, the major ones being acetone and 2-butanone, and these are present in significant concentrations in the condensate water, even after hydantoin formation has been completed (4). The ratio of acetone to 2-butanone was between 3 and 4 in the condensate water samples obtained from lignite (Indian Head, ND) gasification. This ratio corresponded closely to the DMH/EMH ratio observed in the condensate water. As much as 95% of the ketones were converted to hydantoins; but, in general, the limiting species in the Bucherer-Bergs reaction occurring in the condensate water is the hydrogen cyanide, owing to its lower solubility in water at the collection temperature. In the high-temperature gasification zone, ammonia and hydrogen cyanide are produced in about a 10 to 1 ratio (8). Carbon dioxide is generated by the reaction of oxygen with carbon in the hot zone and also by decarboxylation in the pyrolysis zone (in the case of low-rank coals).

If the AIB and ISOVAL in the K/T boundary sediments resulted from natural coal gasification via DMH and EMH, then the AIB/ISOVAL ratio should match the acetone/2-butanone ratio in the products from pyrolysis of the type of coal that was heated at the K/T transition. Pyrolysis products from a number of coal samples of different ranks were collected and analyzed in a pyrolysis/devolatilization project at the University of North Dakota Energy Research Center (9). Data from these analyses are given in Table 1. The ratio of acetone to 2-butanone from pyrolysis of the various coals is between 3 and 4 and is not rank dependent. The ratio of AIB to ISOVAL found in the sediment layers above and below the iridium layer at Stevns Klint was 3 and 4, respectively (1). This means that either a bituminous or lower rank coal could have been the source of the ketones which formed the amino acids found in the sediments.

A terrestrial coal source can account for production of a very large amount of amino acids. The total quantity of acetone and 2-butanone produced from coal pyrolysis is significantly large and is rank dependent (Table 1). Low-rank coals gave three times more ketones than bituminous coals. Thus the yield of hydantoins from 1 kg of lignite could have been as high as 4 g, if all the acetone and 2-butanone produced in pyrolysis were converted via a Bucherer-Bergs reaction in a condensed phase. Geothermal or volcanic gasification of a small coal seam of 1 km^2 by 10 m thickness could have generated 6 x 10^7 kg of hydantoins.

A possible mechanism for natural coal gasification is suggested here. Since a low-rank coal may contain as much as 40% water and a high percentage of oxygen that could be converted to carbon dioxide, a source of intense heat is the main requirement for pyrolytic generation of ammonia, hydrogen cyanide, ketones, and carbon dioxide, which are the precursors for the hydantoins. However, ground or stream water may have played a role in furnishing steam, which could have effectively driven the gasification, and also in furnishing a coolant for the gas produced, so that the condensed gases could react to form the hydantoins. A second possibility is discharge and collection of gases into natural water reservoirs overlying the magma intrusion into the coal seam. Hydrolysis of hydantoins to the amino acids may have been microbially catalyzed or may have occurred over a long time period. Utilization of the 2-substituted amino acids by microorganisms is not likely, resulting in high stability for these compounds. Actually, the method for analysis of the sediments involved conditions that may have hydrolyzed hydantoins to the amino acids; therefore, we cannot rule out their existence in the sediments.

The location and extent of the natural coal gasification promises to be as interesting as the search for the alleged bolide collision site has been. One very important fact must be considered. Whereas the iridium anomaly specifically requires a mantle type of volcanic activity (or bolide), any kind of volcanic or magmatic intrusion into a coal field could have been responsible for the amino acid anomaly. Evidence was recently presented for a tectonic uplifting activity (10) and mantle hot-spot doming in the North Atlantic at the K/T transition (11). Alternatively the magmatic event may have been associated with the North American Laramide magmatic trend, such as the Raton, Colorado, area, where large quantities of char were observed (5). Natural coal gasification may have occurred in several localities, since coal deposits as well as geothermal activity were plentiful in the northern hemisphere.

Natural coal gasification may be only indirectly related to the extinctions that occurred at the K/T transition through volcanism or magmatic intrusions that accompanied a general climatic or sea level change scenario. The complex sequence of extinctions related to volcanism, sea level changes, and other global trends was recently reviewed by Officer (12). There is also a possibility that coal gasification may be related to extinctions during a period of intense volcanic activity. Drawing from the Lake Nyos disaster which involved conversion of a relatively small amount of carbon and evolution as carbon dioxide, we could speculate on another possible relationship. Many of the compounds generated as a result of coal gasification are highly toxic. Besides the ammonia and hydrogen cyanide discussed above, hydrogen sulfide is produced in copious amounts; however, the major component of coal gas by weight is carbon monoxide. Toxic compounds such as phenols and carcinogens such as polynuclear aromatics and amines are also formed. Hydantoins are well known as hypnotics and suspected carcinogens. Many of the organic products would have persisted for a long time. Thus the toxicity of coal gasification gases or other products may offer an alternative explanation for some of the extinctions that occurred in this period.

Table 1 Yields of Ketones (micrograms/gram maf coal) from Pyrolysis of Coals

Coal	%C maf	%O (dif.)	Acetone	2-Butanone
Gascoyne Blue	59.8	32	1600	510
Center	70.0	23	1480	440
Indian Head	72.0	22	1420	400
Rosebud	76.3	16	930	320
Sufco	79.2	14	750	250
Illinois #6	77.2	11	500	120

Pyrolysis conditions were the following: heating rate of 45°C/min, max. 850°C, helium atmosphere, -60-mesh particle size, 5-g sample size (9).

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TRACE ELEMENT BEHAVIOR IN GASIFICATION SYSTEMS

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ABSTRACT

Research has been initiated to determine the behavior of trace elements in integrated gasification combined cycle (IGCC) and integrated gasification fuel cell (IGFC) systems. The goal is to identify and model the important physical and chemical transformation mechanisms of seven trace elements (arsenic, chromium, cadmium, mercury, nickel, selenium, and lead) during gasification as a function of coal composition (trace element abundance and association) and gasification conditions. Identification of the reactions and transformations of trace elements is being conducted in laboratory-scale coal gasification systems. This experimental work is coupled with the development of a computer model to predict the state of trace elements in gasification systems and to identify effective control technologies.

INTRODUCTION

Trace element emissions pose a potential problem to two emerging coal gasification electric power generating systems: IGCC and IGFC. The potential problems associated with trace elements are the release of substances that are considered air toxics and the degradation of fuel cell efficiency due to contamination with minor elements. In order to develop effective technologies to control trace element emissions within anticipated regulatory requirements and to ensure the efficient operation of fuel cells, the type and quantity of trace elements emitted from coal gasification-based systems must be determined as a function of system, system conditions, and coal composition.

The fate of trace elements in coals used in IGCC and IGFC systems is closely tied to how the trace elements are associated in the coal and the gasification conditions. Trace elements in coals are associated in several forms, including organic associations, such as salts of carboxylic acid groups and organic coordination complexes, and mineral associations, such as sulfides, sulfates, silicates, phosphates, and carbonates. During gasification, these inorganic elements are partitioned into gases, liquids, and solids. The transformation of these trace elements into the various states and phases depends upon the fundamental characteristics of the elements and their association with minerals and coal particles. Minerals that are not directly associated with coal particles experience a different process environment than minerals that are intimately associated with coal particles during gasification.

Gasification conditions, such as reducing and oxidizing atmospheres, gas phase composition, pressure, and temperature, influence the partitioning of trace elements between various gases, liquids, and solid inorganic components as a function of location in the gasifier. In order to predict the form of the

inorganic species during gasification, it is essential that detailed information on the distribution of major mineral phases and organically associated inorganic elements be determined. This information is critical since the transformations and interactions during utilization impact the partitioning of trace elements. Modeling the transformations using thermochemical equilibrium calculations combined with various chemical and physical constraints to reach equilibrium can be effectively used to estimate the distribution of gas, liquid, and solid components as a function of gasification conditions.

EXPERIMENTAL APPROACH

The predicting of inorganic transformations (major and minor components) during coal combustion has long been the focus of many research programs.[1-3] In the program described in this paper, the predictive techniques that have been applied to combustion are being modified to predict inorganic transformations under gasification conditions. Many of the current trace element predictive techniques are based on the assumption of equilibrium conditions and not on actual kinetically constrained transformations that occur during coal utilization. The approach used in the program is to combine inorganic transformation algorithms and the thermochemical equilibrium calculations.[4,5] These techniques will be developed to predict the particle-size and composition distribution of the resulting coal ash particulate, along with the state of the vapor species at selected conditions for major, minor, and trace constituents.

The predictive techniques being applied to the modeling of trace elements during gasification require state-of-the-art analytical and experimental data. The modeling of trace elements requires particle-size and composition distributions of the trace constituents in relation to the major and minor species in the coal. To provide the necessary data, computer-controlled scanning electron microscopy (CCSEM) is being adapted to include trace element analysis through the use of wavelength dispersive x-ray spectrometers. Although the automated adaptations to the CCSEM technique will require significant development, generalized distributions of the trace elements can be made manually in conjunction with the CCSEM analysis. To generate the essential experimental data, a pressurized drop-tube furnace (PDTF) is being used to simulate coal gasification. Ash and vapor samples produced from the PDTF are characterized by CCSEM with wavelength adaptations for determining trace elements, wavelength and energy dispersive x-ray fluorescence, inductively coupled argon plasma spectroscopy (ICAP), and atomic adsorption (AA). The following sections discuss the three major developments taking place to produce a predictive methodology for trace element emissions during gasification: transformation modeling, microscopic sample characterization, and laboratory-scale coal gasification.

TRANSFORMATION MODELING

A computer model to predict the evolution of major, minor, and trace elements during the gasification of coal is being created based on the algorithm shown in Figure 1. The shaded boxes in Figure 1 represent the inputs required, while the boxes with a drop shadow are the outputs generated from the model.

The first task of the model is to determine the associations of the major, minor, and trace elements in the coal prior to utilization. The association of the elements prior to utilization will affect their phase, size, and composition distribution in the residual ash and gas streams. The three primary inorganic associations are water, organic, and mineral. Water-associated constituents are generally in the form of sulfates or chlorides present in the moisture of a coal particle. The organically associated constituents are generally found as the salts of carboxylic acid groups attached to the carbon matrix and as oxygen replacement (such as organic sulfur). The mineral associations are elements which comprise discrete minerals in the coal (such as clays, carbonates, and sulfides).

Due to the complexity of interaction of the inorganics during coal gasification, the mineral associations are further divided into mineral type, trace, minor and major element content, size, and juxtaposition. Juxtaposition refers to the association of the minerals with the coal and with other minerals. A locked mineral is intimately associated in the coal particle, while a liberated mineral is external to the carbon matrix. The detailed mineral classification is very important because different minerals behave differently. For instance, carbonates will commonly release CO_2. This will result in a greater potential for mineral fragmentation, depending on the system conditions. Clays which contain high levels of moisture may fragment initially due to the release of H_2O from their porous structure. Silicates are much less prone to fragmentation because they lack any of the previously discussed components.

Many of the mineral particles encountered in coal utilization are rarely free from trace and minor components. To predict the transformations of the trace and minor elements effectively, their distribution among the minerals is required. Whether a mineral is locked within the coal matrix or external to the coal can also have a large impact on its transformations. Locked minerals will be much more likely to coalesce with other minerals and organically associated constituents than the liberated minerals. The liberated particles will also experience a slightly different gas environment during coal gasification since they are not intimately in contact with the highly reducing, exothermic reaction of the carbon matrix.

Once a mass balance is performed around the coal input data, it is necessary to determine which of the inorganic components will be vaporized during the initial gasification process. These calculations will be performed with the use of a thermochemical equilibrium program, PHOEBE,[4,5] created at the Energy and Environmental Research Center (EERC). This code is currently being upgraded to include the appropriate trace element phases. With the exclusion of the vaporized species, the remaining constituents will be processed through algorithms for mineral fragmentation, coalescence of both minerals and organically associated species, and shedding of resulting particles.

The fragmentation, coalescence and shedding algorithms will be developed with the aid of data generated in the pressurized drop-tube furnace (PDTF). These algorithms are designed on various frequency distributions for each of the minerals and physical processes. The organically associated species which do not readily volatilize will also undergo coalescence with mineral particles as a function of the surface area of the minerals during coalescence. A portion of the organically associated species also homogeneously coalesces. The

liberated minerals undergo fragmentation, but do not appreciably coalesce with other minerals due to their lack of intimate contact with the coal.

The state of the volatile species at the resultant conditions will then be determined using the PHOEBE code again. The quantity of species that will condense prior to the resultant conditions are calculated from the PHOEBE data. The condensing species will then be homogeneously and heterogeneously condensed. The heterogeneous condensation will be based on the surface area of the particles. The resultant particulate and vapor species will be compiled and manipulated into various composition and size distributions as to the user's discretion. These distributions can be used to determine effective control technologies for a specific coal or to locate a coal compatible to a specific control technology.

Although the emphasis of this model is to aid in the control of trace element emissions, little attention is being given at this time to the effects of size and composition of inorganic ash components on control technologies. Once this model has been tested and verified, the next logical step will be to investigate the control technologies as a function of particulate and vapor properties.

MICROSCOPIC SAMPLE CHARACTERIZATION

Many of the computer models recently developed to predict the evolution of major and minor elements during coal gasification were made possible by the development on a highly quantitative analytical technique for coal analysis, CCSEM.[6] CCSEM provides a particle-size and composition distribution for the mineral contents of a particular coal for twelve major and minor elements. These raw CCSEM data are the primary input to the newest computer models ash formation. The CCSEM data are used in conjunction with a bulk ash determination (x-ray fluorescence or atomic absorption) to determine the content of nonmineral species by mass balance. The goal for trace element modeling is to provide particle-size and composition distributions for the trace elements and a bulk composition containing trace elements similar to the current data produced for major and minor species. The bulk trace element composition has long been attainable by ICAP or AA, and the size and composition distributions are nearly obtainable by combining the current CCSEM technique with wavelength dispersive x-ray analysis capabilities for trace elements.

The standard CCSEM technique uses an energy dispersive spectrometer (EDS) which allows for the simultaneous determination of major and minor species in the minerals. However, the EDS detector is not sufficiently sensitive to trace elements. A wavelength dispersive spectrometer is much more sensitive for trace elements, but can only characterize one element at a time, thus making it impractical for the time-consuming rigors of the CCSEM technique. By combining both detectors during a single analysis, trace, minor, and major elements can be recorded. This procedure is currently being developed, but is not expected to be fully operational until the second quarter of 1993.

In an initial effort to determine the generalized associations of trace elements with minerals, the standard CCSEM procedure is run on a coal. At the completion of each frame of analysis, the operator can locate the specific minerals and reanalyze them with the wavelength dispersive instrumentation.

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The wavelength data analysis can then be manually compared to the standard CCSEM data to correlate the presence of trace elements with specific mineral species. A generalized trace element profile can then be created for a number of coals to be used for data correlations in the model until the more rigorous technique is completed. In addition, the chemical fractionation technique[7] is being used to support the CCSEM by providing data on the general association of the seven trace metals.

LABORATORY-SCALE COAL GASIFICATION

The fate and distribution of trace elements under the effects of temperature, pressure, and gas composition in IGCC systems are important to the emerging technologies. Laboratory-scale experiments performed in the EERC PDTF are being used to study the partitioning of important trace elements and to enable the prediction of trace element emissions for IGCC and IGFC systems.

The PDTF furnace assembly, Figure 2, consists of a 2.875-inch ID alumina tube (55 inches long) with a slightly reduced end, used to support a flow accelerator in a fixed position, nested on top of a tube of the same dimensions (25 inches long). These tubes are concentrically surrounded by a tube of slightly larger dimensions. The tubes are heated externally by high-temperature tube furnaces equipped with Kanthal Super 33 elements. The entire reactor and the heating elements are housed in a water-jacketed pressure vessel. Coal is introduced into the reactor with a carrier gas through a traversing, water-cooled injector located in the center of the tube. Optional, secondary air enters the reactor at the top of the tube and flows through the tube around the injector assembly. The coal residue and process gases travel down the tube in a laminar flow regime and pass through the accelerator where they are collected by a water-cooled, nitrogen-quenching ash collection probe. Various collection devices can be attached to the collection probe to collect the solids. Size segregation of the ash is obtained using a multicyclone or impactor in conjunction with a final filter. A bulk filter is used to collect ash for bulk chemistry. A water-cooled deposition probe can also be inserted, in place of the ash collection probe, to simulate the deposition conditions in a utility boiler. The product gases are monitored on-line by O_2, CO, and CO_2 gas analyzers or are intermittently sampled for a gas chromatograph (GC).

The PDTF can operate at temperatures as high as 1500°C and pressures up to 250 psi. Efforts are currently underway to attach an atomic absorption unit to the exiting gas line to acquire on-line mercury analysis from the furnace. Previous studies in the PDTF have produced very good gasification simulation results. Burnouts in excess of 95% with high carbon monoxide/carbon dioxide ratios have been produced under gasification conditions.

In this initial modeling effort, three coals will be run under multiple temperatures, pressures, gas compositions and residence times. The resultant samples will be collected in a three-stage multicyclone and characterized using scanning electron microscopy, wavelength dispersive x-ray fluorescence, inductively coupled plasma spectrometry, and atomic absorption. The data generated from the PDTF will support the development of the physical interaction algorithms in the model.

CONCLUSIONS

A computer model to predict the transformations of trace, minor, and major elements during coal gasification is expected to be completed by late 1993. This model will generate the particle-size and composition distribution of the inorganic constituents as a function of the original coal content and system conditions. Advances in both analytical and experimental technologies are currently being made to provide added insight into the modeling of these inorganics during coal utilization.

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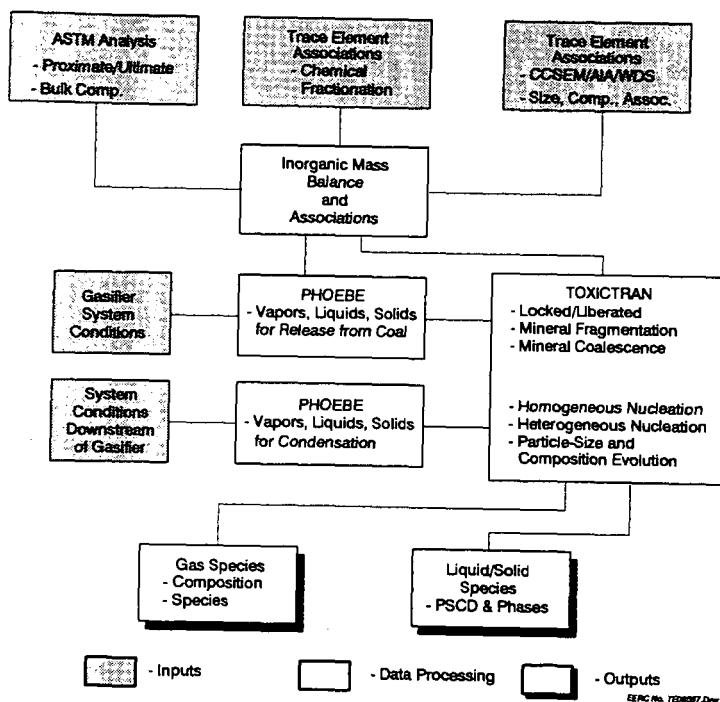
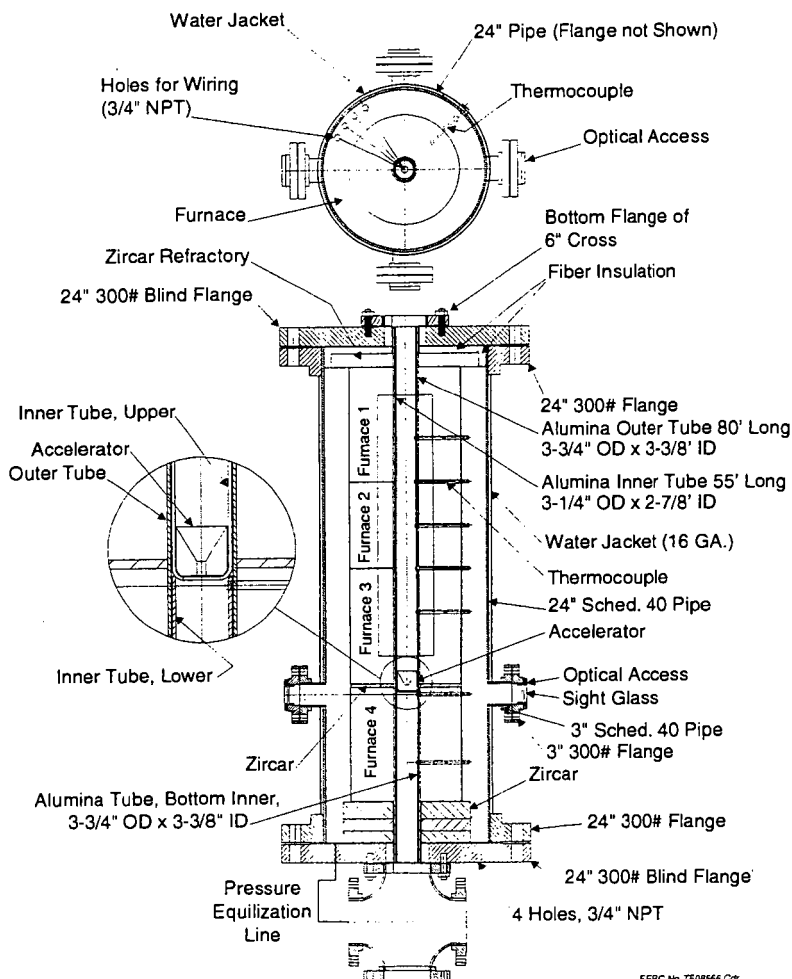Figure 1. Trace element emissions model algorithm.

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Figure 2. Pressurized drop-tube furnace assembly.

TRACE ELEMENT BEHAVIOR DURING COAL COMBUSTION

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ABSTRACT

The emissions of trace elements from coal-powered processes depends to a large extent on the high temperature transformations of the trace species. In a laboratory study utilizing an Alabama bituminous coal, a Wyoming sub-bituminous coal, and a Montana lignite coal, trace element partitioning during coal combustion was examined. Experiments were conducted in an isothermal laminar flow drop tube furnace, using narrowly size-segregated coal samples to minimize particle to particle variation in the feed. In these experiments, the partitioning of the elements Zn, Mn, Cr, As, Sb, and Se among the various size fractions of ash particles was measured as a function of coal type and particle combustion temperature. Different fractions of each element were noted in the submicron ash, with Zn, As, Sb, and Se generally concentrated in the smallest ash particle size fractions.

INTRODUCTION

Title III of the 1990 Amendments to the Clean Air Act identify 189 hazardous air pollutants whose emissions may be regulated [1]. A wide variety of stationary sources, including industrial and institutional combustion sources, are to be regulated as a result of this legislation. Coal-fired electricity-generating utility power plants are currently not regulated by Title III, the hazardous air pollutants portion of the legislation. Pending the results of an EPA study of power plant emissions, however, utility boilers may also be regulated.

Of these 189 hazardous air pollutants, 11 are trace metals contained in coal. For these metals - Sb, As, Be, Cd, Co, Cr, Hg, Pb, Mn, Ni, Se - the concentration in the stack gases strongly depends upon elemental partitioning during coal combustion. For example, volatile elements such as Hg are likely to leave the boiler with the flue gases, whereas relatively non-volatile elements such as Mn are likely to be collected with the fly ash or bottom ash. These are not firm "rules", however; for any element, variations in concentration in the various effluent streams have been reported [2-5].

Many of the observed differences in partitioning have been attributed to differences in coal type. This is likely due to differences in the form of an element in coal with rank. Elements associated with clays generally associate with fly ash, whereas elements associated with the organic matrix are more likely to volatilize. Consider chromium as an example. A typical chromium concentration in U.S. coal is 15 to 20 ppm [6,7], with the elemental forms uncertain. One study identified Cr within clays as a possibility, while another suggested that

50% organic association was possible [4,6]. These differences point to possible differences in partitioning for this element.

To investigate the importance of coal rank, and therefore indirectly investigate the effect of the elemental form on partitioning, a detailed laboratory study was conducted. In this paper, results from three U.S. coals are presented.

EXPERIMENTAL

Coal Selection
Experiments were conducted with three different parent coals: Illinois #6 and Alabama Rosa (bituminous), Wyoming Comanche (sub-bituminous), and a Montana lignite. A density-separated sample of the Montana lignite, treated to remove all coal particles with a specific gravity greater than 1.8, was also investigated to look for differences in behavior arising from reduced ash content. Selected trace element concentration data for these coals are presented in Table I. For most of the elements considered in this study, concentration of the element within the coal varied by factors of 2 to 20 with coal type.

Laboratory Combustion Facility
All of the coal combustion experiments were conducted in the MIT laboratory scale laminar flow furnace [8]. A schematic diagram of this facility is presented in Figure 1. Coal particles, sized to 53/63, 75/90, or 125/150 μm by dry sieving techniques, were injected at the top of the reactor through a water-cooled feeder probe. Feed rates of 0.01 to 0.03 g/min were used, with nitrogen serving as the entraining carrier gas. Combustion occurred in the heated zone of the laminar flow reactor, with coal particle temperatures controlled by the concentration of oxygen in the bulk gas. Reactor wall temperatures were held constant at 1750 K. At the conclusion of combustion, all ash particles and gaseous combustion products were extracted with a water-cooled, nitrogen-quenched sampling probe. Nitrogen gas was also transpired through a porous metal probe liner to minimize particle losses during sampling. Particles were size segregated on-line as needed through the use of an Andersen Mark 2 eight-stage cascade impactor.

Chemical Analysis
Neutron activation analysis at the M.I.T. Nuclear Reactor Laboratory was used to determine the concentration of trace elements in all coal and ash samples examined in this study. Analysis of orchard leaves, a standard reference material obtained from NIST, was used for calibration.

RESULTS AND DISCUSSION

The variation in the concentration of selected trace elements in the submicron ash was examined as a function of coal type, coal particle size, and coal particle combustion temperature. In addition, the concentration of selected trace elements as a function of ash particle size was examined.

Trace Element Concentration as a Function of Ash Particle Size

The concentration of trace elements as a function of ash particle size was examined in a study of Wyoming Comanche sub-bituminous coal. A 75/90 μm size fraction of the coal was used in these tests. Furnace wall temperature was maintained at 1750 K, with an oxygen partial pressure of 0.30 atmosphere (balance nitrogen). Trends observed for the elements vanadium, chromium, and manganese are presented in Figure 2. Vanadium was uniformly distributed among all particle size classes, whereas chromium was slightly enriched and manganese was significantly enriched in the submicron fraction of the ash. Chromium concentrations measured for ash generated from combustion of the density segregated Montana lignite in 20% oxygen show a similar trend to the chromium from the Wyoming coal.

Enrichment in the smallest size fraction is generally taken as a sign of vaporization. This is because condensation occurs preferentially on the smallest ash particles that provide most of the surface area. Non-volatile elements generally are concentrated in the largest ash particles. The concentration of Sc, presented for comparison in Figure 2, shows behavior typically associated with a highly refractory, non-vaporizing element. From this, we conclude that for the Wyoming sub-bituminous coal, 1) manganese vaporizes during combustion and condenses on the smallest ash particles; 2) chromium may partially volatilize during combustion; and 3) vanadium remains associated with the larger fly ash particles and hence is relatively non-volatile.

Effect of Combustion Temperature

At the gas temperatures considered in this study, the combustion of pulverized coal is controlled by the diffusion of oxygen to the particle surface at the gas. The rate of combustion and hence the coal particle temperatures are therefore affected by the flux of oxygen to the surface, which in turn is controlled by the partial pressure of oxygen in the gas. Thus, by increasing oxygen partial pressure, the coal particle combustion temperature can be raised accordingly. Measurements and calculations have indicated that coal particle temperatures may increase from approximately 1900 to 2000 K in 20% oxygen to as high as 2600 to 2800 K in 80% oxygen [8].

The effect of coal particle combustion temperature on trace element concentration in the submicron ash was investigated in a study of the Wyoming coal. Results obtained for the elements V, Cr, As, and Sb are presented in Figure 3. Concentrations of Sc are again presented as an example of anon-volatile element. Vanadium, chromium, and scandium concentrations all increased with increasing oxygen concentration indicative of relative non-volatility. Arsenic and antimony concentrations, however, decreased with increasing temperature. This suggests that the majority of each of these elements vaporized at relatively low temperatures. The reduction in concentration is a diluent effect, resulting from additional vaporization of refractory species at higher temperatures.

Effect of Feed Coal Particle Size

Trace element concentrations in the Montana lignite coal and combustion-derived submicron ash as a function of coal particle size are presented in Figure 4. Little difference was noted in the concentration of these elements in the coal or the ash for most elements. Chromium concentrations in the submicron ash, however, decreased as larger coal particles

were burned. This suggests that chromium in the largest coal particles was either retained by aluminosilicate minerals (ash particles), or was present in a more refractory form initially.

Effect of Coal Type
Enrichment of trace elements in the submicron ash was examined for the three parent coals considered in this study. As shown in Figure 5, enrichment was typically lowest for the sub-bituminous coal. Arsenic and vanadium were most volatile in the bituminous coal, whereas chromium was most volatile in the lignitic coal. For a given element, differences in enrichment factor as a function of coal type suggest differences in volatility. This in turn suggests differences in the predominant form of the element in the parent coals.

ACKNOWLEDGEMENTS

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Table 1. Coal Trace Element Data

	Alabama Bituminous (75/90 μm)	Wyoming Sub-bituminous (75/90μm)	Montana Lignite (75/90 μm)	Density-Graded M. Lignite*
Ash (wt%, dry)	7.3	5.2	6.9	5.9
Trace elements (ppm by weight of coal)				
Mn	20	25	78	66
Cr	14	11	3.8	6.1
As	30	1.6	4.0	-
Sb	1.4	-	0.6	-
Se	-	-	0.5	-
Co	9.2	2.4	0.9	-
V	17	16	5	-
Zn	23	-	8	-
U	-	0.9	0.5	-

Figure 1. Laminar-entrained flow reactor used for combustion experiments.
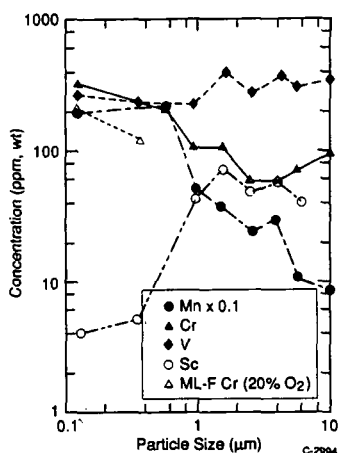
Figure 2. Concentration of trace elements in ash as a function of ash particle size for Wyoming and Montana coals. 75/90 μm, 1750 K, 30% O_2 except as noted.
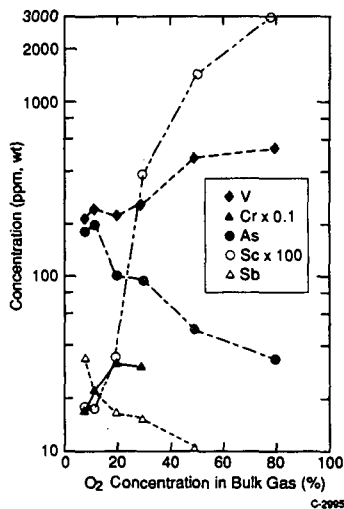
Figure 3. Concentration of trace elements in ash as a function of oxygen partial pressure. Wyoming coal, 75/90 μm, 1750 K.
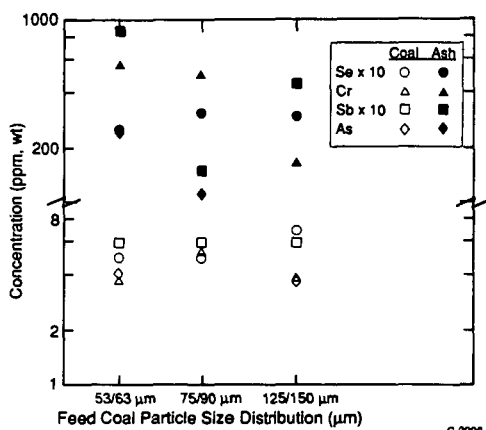
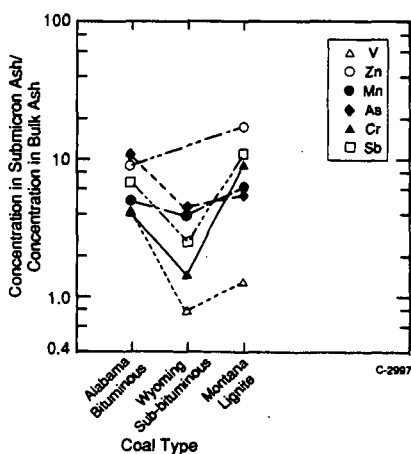Figure 4. Concentration of trace elements in Montana lignite coal and ash as a function of coal particle size. 1750 K, 20% O_2.

Figure 5. Relative concentration of trace elements in submicron ash as a function of coal type. 75/90 μm, 1750 K, 30% oxygen except Montana coal (20%).

FORMS OF OCCURRENCE OF ARSENIC IN COAL
AND THEIR BEHAVIOR DURING COAL COMBUSTION

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ABSTRACT

New information from XAFS spectroscopy on the occurrence of arsenic in U.S. bituminous coals shows that arsenic may be present in one or more of three distinct forms: (i) arsenical pyrite; (ii) arsenopyrite (FeAsS); and (iii) arsenate (AsO_4^{3-}), most probably as a result of oxidation. In ash samples analyzed to date by XAFS spectroscopy the arsenic is present predominantly as arsenate species. Some preliminary data on arsenic capture efficiency during combustion suggest that the presence of arsenate in the coal may facilitate the retention of arsenic in combustion solids.

INTRODUCTION:

A recent comprehensive study of ash formation during combustion of U.S. coals [1] has indicated the importance of the form-of-occurrence of an element in the coal for determining the behavior of major elements during pulverized coal combustion. Similarly, information regarding the forms of occurrence of minor and trace elements in coal and ash must also be obtained to understand their behavior during combustion and to assess whether or not the release of these elements during combustion poses a significant environmental hazard. One of the more critical trace elements in this regard is arsenic as its behavior can be variable. For example, large variations (from <1% to >50% of the total arsenic flux) were reported for arsenic concentrations in the vapor phase at a U.S. power station [2]; and, in trace-element mass balance studies at commercial power plants, arsenic in bottom ash has been shown to vary from as little as 0.5% to as much as 10% of the total arsenic, with the balance in fly ash, except for a very small fraction (<0.5%) that escapes in the flue gas [3]. It is likely that one of the more important factors that might influence the behavior of arsenic during combustion is the form of occurrence of arsenic in the coal.

In his comprehensive review of trace elements in coal, Swaine [4] lists the probable major forms of occurrence of arsenic as arsenical pyrite and arsenopyrite (FeAsS) based on observations (and speculations) made on various coals from around the world. In the U.S., there have been a few direct observations made on the forms of occurrence of arsenic in coal: such observations have been made using scanning electron microscopy [5,6], the electron microprobe [7,8], and other less direct methods [9]. These findings by and large confirmed the occurrence of arsenic as arsenical pyrite in most U.S. coals. In recent work [10,11], we have demonstrated the potential of XAFS spectroscopy as a direct and nondestructive probe for forms-of-occurrence information about trace elements in coal and ash down to concentration levels as low as 10 ppm. In this study, we will present new data on arsenic occurrences in various U.S. coals and derived ash materials.

EXPERIMENTAL:

Samples: Various coals from the Argonne Premium coal sample bank (APCSB), from the Department of Energy Coal Sample (DECS) bank administered by D. Glick and A. Davis (Pennsylvania State University), and from miscellaneous sources were used in this study. Ash samples were prepared from some of these coals in a drop-tube furnace at PSI Technology (PSIT) Company or in a larger-scale combustion unit at the University of Arizona (UAZ). The drop-tube furnace was run at 1750 K and an oxygen content in the furnace atmosphere of either 7% or 10.5%. Ash samples were collected on filters; in the case of the UAZ combustion unit, an Anderson impactor was used to segregate the ash particulate matter by size. Arsenic contents of the coals were determined by either instrumental neutron activation analysis (INAA) or by proton induced x-ray emission (PIXE), although we have relied on published INAA analyses [12] for the arsenic contents of the APCSB coals. The same techniques were also used to determine the arsenic contents of ash samples.

XAFS Spectroscopy: XAFS spectroscopy was performed at beam-line X-19A at the National Synchrotron Light Source, Brookhaven National Laboratory. For arsenic in coals and ash samples, the absorption of X-rays was measured over the spectral range from 11.75 keV to as high as 13.0 keV; over the XANES region (11.85 to 11.90 keV), absorption data were collected every 0.25 eV. Absorption of the X-rays was measured by means of a thirteen-element germanium array detector [13] that detected the fluorescent X-rays only in a specified tunable energy window that corresponded to the energy of the arsenic fluorescent K_α X-rays. The arsenic K-edge XANES spectra shown in this report are calibrated with respect to a zero energy point (11.867 keV) defined as the position of the white line in the spectrum of As_2O_3 that was run simultaneously with all arsenic spectra. Other details of XAFS experimentation for trace element studies are given elsewhere [10,11].

RESULTS AND DISCUSSION:

Arsenic in Coal:

Preliminary XAFS work on the speciation of arsenic in coal [10,11] has shown that it is relatively easy to distinguish among the different arsenic oxidation states likely to be found in coals and other geological materials. This work showed that arsenic was present either in association with iron as in arsenical pyrite, in which arsenic substitutes for sulfur in the pyrite structure, or as an arsenate (AsO_4^{3-}) species, presumably formed as a result of oxidation.

However, it is also essential for speciation studies of arsenic in coal to be able to distinguish between the discrete arsenic mineral, arsenopyrite (FeAsS), and arsenical pyrite (FeS_2). These two forms-of-occurrence of arsenic have been postulated to be the likely major forms of arsenic in coal [4]. The As K-edge XAFS spectra of arsenopyrite and arsenical pyrite are quite similar, but there are subtle differences that can be used to discriminate successfully between these alternatives in both the XANES and EXAFS regions of the spectra. Figure 1 compares the XANES and radial structure function (derived by Fourier transform of the EXAFS function, k^2.CHI) spectra from the two materials. There are clearly more distinctive features, in both magnitude and structure, in the radial structure function (RSF), which is the most processed of these spectra. But even in the XANES spectra there are sufficient differences to discriminate between arsenopyrite and arsenical pyrite simply by inspection.

Such distinctions can be seen in arsenic XANES spectra of coals down to at least 10 ppm. Figure 2 shows the normalized XANES spectra of arsenic in three coals that vary in arsenic content from 17 ppm to 434 ppm. Of these coals, the Pittsburgh seam coal is unique in that its XANES spectrum is closely similar to that of arsenopyrite, whereas the remainder of the coals have features consistent with As in solid solution in pyrite. For the two coals richest in arsenic,

the radial structure functions are shown in Figure 3 and, upon comparison with the RSFs shown in Figure 1, the RSF spectra confirm the inferences based on the XANES spectra. As indicated by the extra white-line peak in the XANES spectrum and also by the peak at about 1.4 A in the RSF, the Jefferson coal contains a significant fraction of its arsenic as arsenate. Even with this complication, it is clear that remainder of the arsenic in this coal is present in substitutional form for sulfur in pyrite.

XAFS spectra of arsenic were reported previously [10,11] from a suite of float/sink fractions from newly opened vials of the APCSB Upper Freeport coal and showed that the dominant arsenic form-of-occurrence was arsenical pyrite. Similar XAFS spectra were also obtained from the same samples after a three month interval, during which time the samples were stored in glass (not air-tight) vials, and from previously opened vials that had been opened for a number of months. The spectra of these samples were found to be significantly different from those obtained previously. As can be seen from Figure 4, the arsenate contents of these Upper Freeport coal fractions are significantly higher after just three months' storage at room temperature in closed glass vials. These observations confirm that the oxidation of arsenical pyrite to arsenate can occur extremely rapidly, even during storage at room temperature.

The data presented here and in previous preliminary studies show that there are at least three forms of occurrence of arsenic that may be found in laboratory samples of U.S. coals. Based on the limited number of samples examined to date, arsenical pyrite appears to be the most common of these forms, with arsenate as the next most common (although it is conceivable that this form is only formed as a result of oxidation during processing and storage), and arsenopyrite as the least common.
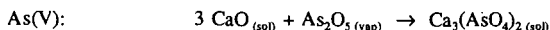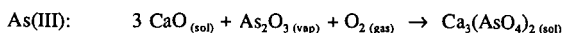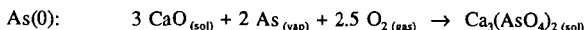
Arsenic in Ash:

The conversion of arsenic forms in coal to arsenic forms in ash as a result of combustion has been investigated for a number of ash samples prepared in the drop-tube furnace at PSIT Company or the combustion unit at UAZ. All of the ash samples derived from coal combustion that have been examined to date by XAFS spectroscopy contain arsenic predominantly, if not entirely, in the form of arsenate (AsO_4^{3-}) complexes. Such complexes are readily recognized by the strong white line absorption at about 3 - 4 eV and the broad low intensity peak that is a maximum in the range 80 - 90 eV in the As XANES spectrum, and by the major peak at about 1.3 - 1.4 A in the RSF of samples rich in arsenic. Figure 5 shows the As K-edge XANES spectra for the bottom ash collected in the UAZ combustion unit from combustion of Kentucky #9 coal and of the fly-ash samples collected in the same unit on an Anderson impactor, during combustion of Beulah (ND) lignite. In comparison to arsenate complexes of known crystal structure, the arsenic K-edge XANES spectra of this and similar bottom ash samples are relatively featureless: the white-line peak is relatively broad and there are no minor peaks in the 10 - 30 eV range and no obvious shoulders or inflection points on the broad peak in the range 50 - 100 eV. Such a lack of features is consistent with a mixture of different structural environments for arsenate complexes in these materials, such as those that might be expected if the arsenate complexes were assimilated in amorphous or glassy materials.

The spectra of the fly-ash samples collected in the UAZ combustion unit on an Anderson impactor, during combustion of Beulah (ND) lignite, begin to deviate from this pattern, particularly for the finer of the two fractions. In the spectrum of the fine fraction, the width of the white line is narrower and there is the obvious presence of a minor peak at about 20 eV in comparison to the coarse fraction. These observations are interpreted as indicating a significantly higher fraction of a crystalline arsenate occurrence in the finer fly-ash fraction than in the coarse fly-ash fraction.

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Recent observations and theories on ash particulate formation involving major elements during pulverized coal combustion [1] have invoked two main mechanisms for ash particle formation: (1) evaporation of volatile species and condensation of phases from the vapor, and (2) partial or total fusion and agglomeration of mineral particles. The first mechanism commonly results in the formation of small particles of relatively well defined composition and crystallinity, such as alkali and alkaline-earth sulfates. The second mechanism results in the formation of partially molten aluminosilicate particles that incorporate varied amounts of basic elements. These latter particles tend to be much larger and are generally at least partially amorphous (glass) upon quenching. In such partially molten deposits, it is likely that AsO_4^{3-} species would be incorporated as a network former in aluminosilicate melts, in much the same way as phosphate anionic species (PO_4^{3-}) are incorporated in such melts.

Alkaline-earth orthoarsenates are relatively stable compounds (calcium orthoarsenate melts only at temperatures above 1450°C and magnesium orthoarsenate would be expected to be almost as refractory) and consequently they are prime candidates as condensates from vapor phase arsenic species during combustion, especially of low-rank coals. Under combustion conditions, decomposition of arsenical pyrite or arsenopyrite will be rapid and release arsenic vapor, which should then readily oxidize to vaporous arsenic oxides. In the presence of oxygen, the following solid-vapor reactions will lead to the condensation of calcium orthoarsenate, depending on the oxidation state of arsenic in the vapor phase:

$$As(0): \quad 3\ CaO_{(sol)} + 2\ As_{(vap)} + 2.5\ O_{2\ (gas)} \rightarrow Ca_3(AsO_4)_{2\ (sol)}$$

$$As(III): \quad 3\ CaO_{(sol)} + As_2O_{3\ (vap)} + O_{2\ (gas)} \rightarrow Ca_3(AsO_4)_{2\ (sol)}$$

$$As(V): \quad 3\ CaO_{(sol)} + As_2O_{5\ (vap)} \rightarrow Ca_3(AsO_4)_{2\ (sol)}$$

It is apparent that these reactions become simpler and involve fewer molecular species with increasing oxidation state of the arsenic. In particular, regardless of whether the transitory species in the vapor phase is the oxide, As_2O_5, or the anion species, AsO_4^{3-}, no additional oxygen is necessary in reactions involving the As(V) oxidation state as a reactant. Hence, the presence of arsenate in the coal might be expected to facilitate the formation of arsenate compounds during combustion and its capture on particulate matter. Furthermore, arsenate mineral species that are not associated with pyrite or arsenopyrite particles in the coal need not undergo vaporization, but may remain as discrete particles or be assimilated by partial fusion into other particles during combustion.

Comparison of the arsenic retention during combustion for the two DECS coals in the PSIT drop-tube experiments is tabulated below:

Coal	As (coal)	As (ash)	Wt% Ash	As cap. eff.[1]
Pittsburgh	70	31	10.0	0.04
Illinois #6	10	21	14.5	0.30

[1]Arsenic capture efficiency is defined as: As (ash)/(As(coal)/Wt fn. ash)

It can be seen from this table that relatively little of the arsenic is captured on the filter and it is probable that arsenic in both vapor and submicron microparticulate matter may have avoided

the filter sampling process. From this tabulation, it would appear that the arsenic is captured more efficiently in the case of the Illinois #6 (DECS-2) coal than the Pittsburgh (DECS-12) coal. Although this would appear to be consistent with anticipated trends based on the forms of occurrence of arsenic in the original coals (the Pittsburgh coal contains virtually all arsenic as arsenopyrite, whereas about 40-50% of the arsenic in the Illinois #6 coal is oxidized to arsenate), it may be fortuitous because other factors in the combustion experiment and sampling process that might influence arsenic capture have not been considered.

CONCLUSIONS:

XAFS spectroscopy has identified three distinct arsenic occurrences in U.S. bituminous coals: (i) arsenical pyrite; (ii) arsenopyrite; and (iii) arsenate species, which may have formed from the other two forms by oxidation. This technique also indicates that, regardless of the original form of occurrence of arsenic in coal, all arsenic forms are oxidized to arsenate forms during combustion of coal. The presence of arsenate forms in the original coal may facilitate the retention of arsenic in ash; however, more work needs to be done to prove this point adequately.

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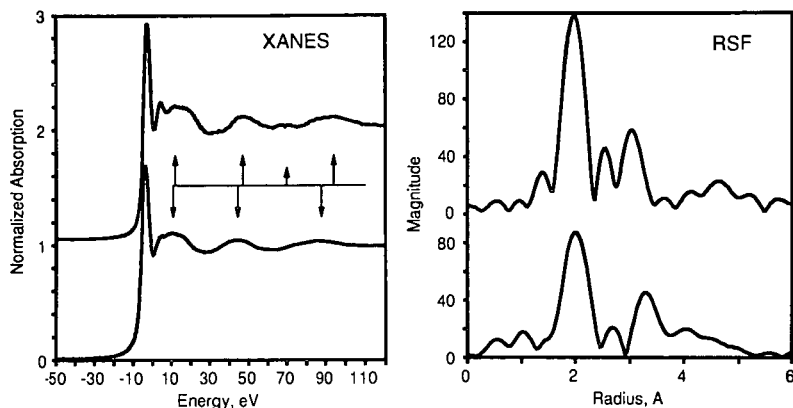
Figure 1: Comparison of XANES and RSF spectra for arsenic in arsenical pyrite (top) and arsenopyrite (bottom).
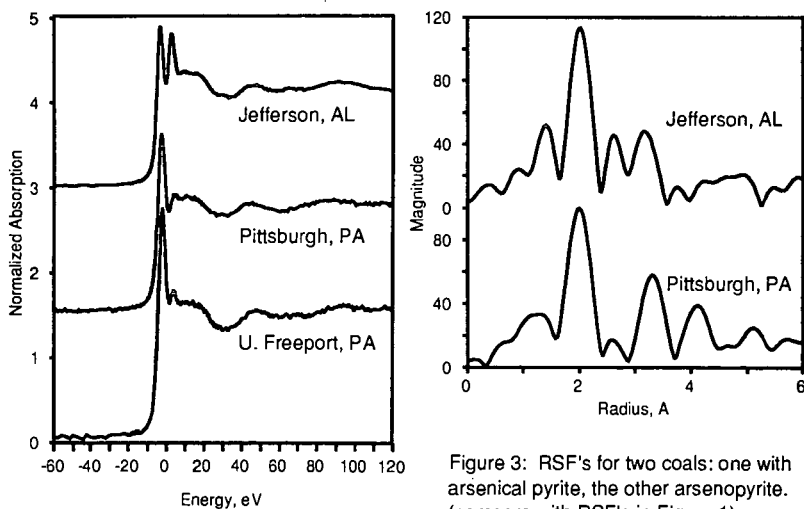

Figure 2: Arsenic K-edge XANES spectra for three U.S. bituminous coals

Figure 3: RSF's for two coals: one with arsenical pyrite, the other arsenopyrite. (compare with RSF's in Figure 1).
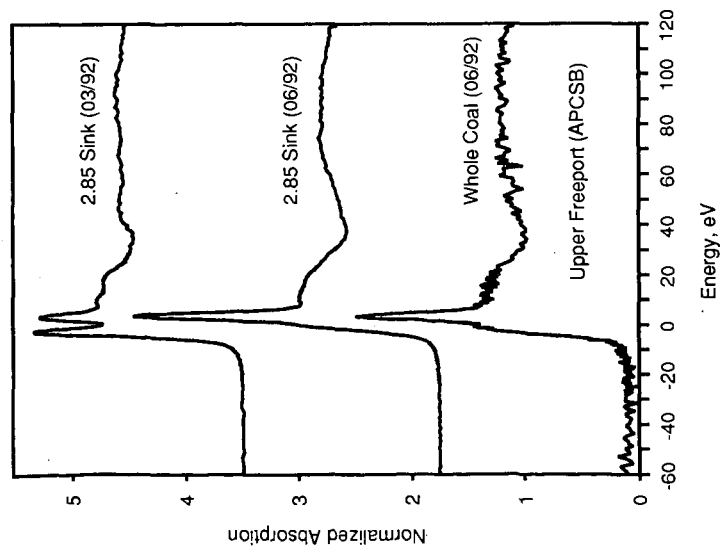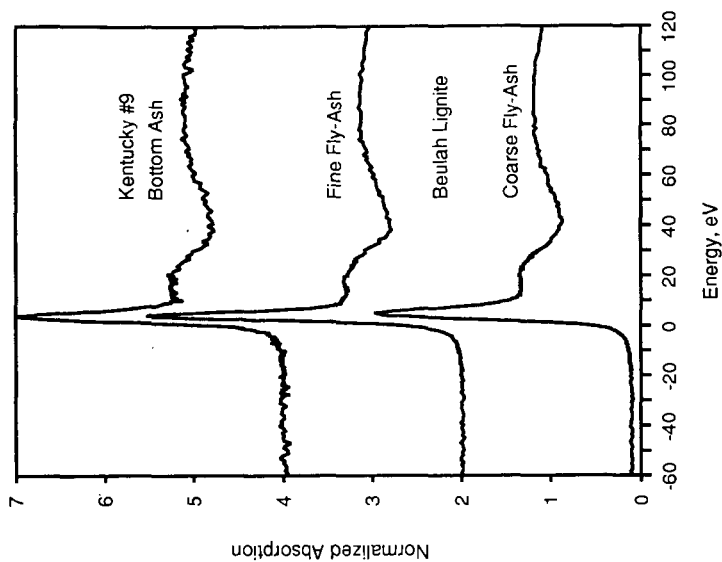
Figure 5: Arsenic K-edge XANES spectra for ash samples collected in the University of Arizona combustion unit.

Figure 4: Arsenic K-edge XANES spectra for oxidized coals. (compare bottom spectra with that in Fig. 2)